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(54) Title: CONTRAST COLORANT FOR PHOTOPOLYMERIZABLE COMPOSITIONS

(57) Abstract

A contrast colorant for photopolymerizable composition containing an addition polymerizable photoinitiator and a polymerizable monomer capable of photopolymerization initiated by the photoinitiator, which colorant comprises a leuco triarylmethane dye and a bromine or chlorine substituted neoalkane or cycloalkane as photoactivator for formation of the colored form of the dye.

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CONTRAST COLORANT FOR PHOTOPOLYMERIZABLE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

In the manufacture of printed circuit boards by the subtractive process, the process involves adhering a photopolymerizable film to the surface of a copper-clad laminate while covering the photopolymerizable layer with a protective film or support. Upon exposure to light in accordance with a predetermined pattern, those portions of the photopolymerizable layer exposed to the light form a solvent resistant pattern, while the unexposed portions may be readily washed away. The exposed copper layer may then be etched or plated.

The dry, photopolymerizable photoresist films are typically light in color and transparent. When viewed in relation to the underlying copper surface, it is extremely difficult to be able to determine the presence or absence of the film, so as to assure that the circuit design has been accurately delineated on the copper plate. In order to aid in the inspection of the photoresist layer, a number of different dye systems have been taught for incorporation in the photopolymerizable layer.

There are many considerations, both as to operability and practicality, in the choice of the dye systems. The dye system should allow for a clearly observable layer when in contact with the copper plate. Furthermore, the dye system may not significantly interfere with the curing of the layer upon exposure to light. The dye may interfere by absorbing light, so as to prevent light penetration through the layer or acting as a free-radical polymerization inhibitor, so as to react with free-radicals to terminate chains. In addition, the dye system should not be unduly sensitive to heat, base or acid, so that it may remain stable for long periods of time during storage, as well as during processing. Otherwise, if the dye has been subject to extensive degradation prior to curing of the photoresist, the observed color will be faint and not readily discernible.

Description of the Prior Art

In view of the numerous patents which have issued in the field, only the more relevant ones will be cited. U.S. Patent No. 4,065,315 has an extended discussion of dyes, and discloses the combination of an organic halide capable of liberating halogen free-radicals on exposure to actinic light in combination with the free base of triarylmethane dyestuffs. In this patent, there is an extended discussion of the relevant prior art. U.S. Patent No. 3,113,024 teaches the heat sensitivity of triarylmethane bases with certain active halides.

SUMMARY OF THE INVENTION

Print out dye systems are provided for use in photopolymerizable composition, particularly as photoresist layers on copper surfaces. The print out dye system comprises in combination, the leuco form of a triarylmethane dyestuff with a thermally stable, light-sensitive, non-aromatic polyhalo compound having at least one halo of atomic number 17 to 35, being alicyclic or

neoalkyl and substantially free of geminal halogen substitution. The print out dye system is incorporated into a photopolymerizable composition comprising a polymeric binder, at least one addition polymerizable monomers, at least one photoinitiator, normally a small amount of a dye contrasting with the colored form of the triarylmethane dyestuff, and minor amounts of other additives. Upon exposure to actinic light, the print out dye system develops a distinctive colored layer readily distinguishable from the uncured photopolymerizable composition and copper underlayer, which cured layer is stable during development, plating and etching treatments.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

In accordance with the subject invention, a novel print out system is provided which involves a combination of a triarylmethane leuco dyestuff and a polyhalogenated compound, free of halogen geminal substitution, containing at least one halo atom of atomic number 17 to 35 and which is non-sublimable and boils at greater than 200° C. at atmospheric pressure. The halogen compound is a substituted cycloalkane or neo-alkane. The print out dye system will normally be used incorporated in an addition polymerizable composition involving a polymeric binder, at least one addition polymerizable monomer, usually involving combinations of monomers, having one or a plurality of addition polymerizable ethylenic groups, a photoinitiator, a dye having a color contrasting with the colored form of the triarylmethane dye, solvents and minor amounts of other materials. The photopolymerizable composition should be relatively free of oxidants, for example, peroxides.

The subject composition as photoresist formulations are found to be stable for long periods of time, under normal storage conditions as well as upon storing in contact with copper surfaces. In addition it is

stable during development in both aqueous and non-aqueous developers, as well as in acid or alkaline plating environments. The leuco dye print-out system, which has virtually no effect on the separate photopolymerization reaction, reaches maximum density within 60 seconds after exposure.

In describing the subject invention, the print out system will be considered first, followed by the various elements of the photopolymerizable system.

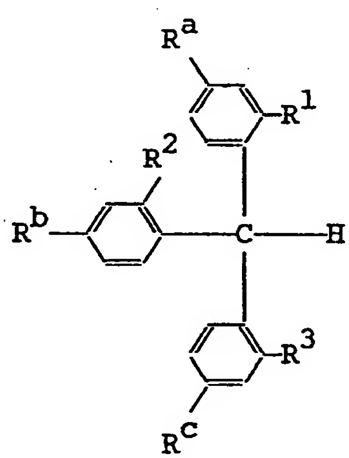
The print out system has in combination a leuco triarylmethane dye and a polyhalogenated hydrocarbon, which is either alicyclic, particularly cyclohexane, or neo-alkane, particularly neopentyl, wherein the halogenated compounds are free of geminal substitution. The halogens will be of atomic number 17 to 35, there being at least one bromine, more usually at least two bromines and preferably greater than 50 percent of the halogen in the molecule being bromine. The amount of halogenated compound will be under the conditions of exposure sufficient to react with the leuco triarylmethane dye to form a sufficient amount of the colored version of the triarylmethane dye.

The mole ratio of the triarylmethane dye to halogenated compound will vary with the nature of the halogenated compound. Usually, the mole ratio of dye to halogenated compound will generally be in the range of about 0.2-5, more usually 0.5-2. Usually there will be about 0.01 to 3, more usually about 0.1 to 2, and preferably about 0.5 to 2 parts by weight of halogenated compound per part by weight of dye.

The leuco triarylmethane dyes will have the tertiary carbon atom bonded to hydrogen and the individual phenyl rings may be substituted or unsubstituted, usually having not more than about two substitutents per ring, more usually having not more about one substituent

per ring, which will usually be ortho or para, more usually para. The substituents may be joined to provide polycondensed systems, such as xanthenes, acridine, and the like. The substituents may be amino (including mono- and dialkyl amino, wherein the alkyl groups are from 1 to 6, usually from 1 to 2 carbon atoms), oxy, hydroxy or alkoxy, particularly alkoxy, wherein the alkoxy group is of 1 to 6, usually of 1 to 2 carbon atoms, halo of atomic number 9 to 80, usually 9 to 35, alkyl of from 1 to 6, usually from 1 to 2 carbon atoms, non-oxo-carbonyl, nitro, sulfo, acyl, or the like. The substituents will be chosen based on convenience, lack of interference with the photopolymerizable system, the desired color, thermal and oxidative stability under the conditions of use, and other practical considerations. The particular choice of the substituents on the triarylmethane leuco dye may be varied widely within the subject invention.

For the most part, the leuco dyes of this invention will having the following formula:



wherein:

R^{a-c} may be the same or different, and will generally be hydrogen, amino, including mono, and dialkyl amino, wherein the alkyl groups are from 1 to 6, usually from 1 to 2 carbon atoms, oxy, including hydroxy or

alkoxy, preferably alkoxy, wherein alkoxy is of from 1 to 6, usually from 1 to 2 carbon atoms, non-oxo-carbonyl of from 1 to 6, usually 1 to 4 carbon atoms, halo of atomic number 9 to 80, usually 9 to 53, and preferably 17 to 53, alkyl of from 1 to 6, usually of from 1 to 3, and more usually from 1 to 2 carbon atoms, cyano, nitro, or the like;

R^{1-3} may be the same or different and may be the same or different from R^{a-c}, R^{1-3} more usually being hydrogen or R^2 taken together to form a ring having a carbon atom or heteroatom, e.g. N, O and S.

Preferred groups for R^{a-c} are amino, dialkyl amino, wherein alkyl is of from 1 to 3, usually 1 to 2 carbon atoms, alkoxy of from 1 to 3, usually 1 to 2 carbon atoms, or chloro, more preferably there being at least 1, usually 1 to 2, and more usually 1 to 3, amino groups, including alkyl and dialkyl amino for R^{a-c}.

Illustrative leuco dyes include crystal violet, malachite green, basic blue, pararosaniline, rosaniline, patent blue A or V, or the like.

The halogenated compounds which are the other member of the print out dye composition are either cycloalkanes or neoalkanes, boiling at atmospheric pressure above about 200°C., having at least one bromine or chlorine, preferably at least two bromine atoms, wherein heterosubstituents are other than geminal, is stable under processing conditions, but is able to undergo bond clevage during irradiation with light, and is otherwise stable prior to the light irradiation, and does not adversely interfere with the photopolymerization.

The bromocycloalkanes will for the most part have the following formula:

$$CHX(CHY)_n$$

wherein:

X is bromine or chlorine, usually bromine;

the Y's may be the same or different and are hydrogen, bromine, or chlorine, usually at least 1 Y being bromine, and preferably there being from n-2 to n halogens which are chlorine or bromine; and

n is 4 to 7, preferably 4 to 5. Particularly preferred is the compound of the formula:

$$(CH)_6(Br)_{6-m}Cl_m$$

wherein:

m is 0 to 3, preferably 0 to 2, more preferably 1.

The neo-alkanes will for the most part have the following formula:

$$C(CH_2X)_p(CH_2Z)_{4-p}$$

wherein:

X is bromine or chlorine, usually bromine;

Z is hydrogen or hydroxyl; and

p is 1 to 4, usually 2 to 4, preferably 2, particularly wherein Z is hydroxyl, or 4.

Illustrative halogenated compounds include 1, 2, 3, 4, 5-pentabromo-6-chlorocyclohexane, dibromoneopentyl gylcol, or pentaerythrityltetrabromide. That is, the halogen should be bonded to a carbon having from 1 to 2 hydrogen atoms.

Turning now to a consideration of the addition polymerizable composition, particularly the photoresist composition, containing the print out dye compositions of this invention, the film will normally have from about 40 to 80 weight percent of a polymeric binder, from about 15 to 30 weight percent of one or more monomers, from about 0.001 to 10 percent by weight of polymerization free

radical initiator or photoinitiator, from about 0.01 to 2 weight percent of the leuco triarylmethane dye, from about 0.1 to 4 weight percent of the halogen containing compound, from about 0.01 to 0.1 weight percent of a colored dye contrasting with the leuco dye, and from about 0.001 to 5 weight percent of various additives, such as plasticizers, antioxidants, fillers, thixothropic, leveling agents, and adhesion promoters. If desired, pigments can also be included.

The next to be considered will be the cross linking monomer, which may vary widely, and may have from 1 to 4, usually 1 to 3, preferably 2 to 3, addition polymerizable olofinic groups. The following addition polymerizable olofins are illustrative of compounds which find use.

Suitable compounds which can be used alone or in combination include the alkylene and polyalkylene glycol diacrylates prepared from alkylene glycols having two to fifteen carbon atoms or polyalkylene ether glycols of one to ten ether linkages. Outstanding materials are ethylenically unsaturated groups, especially vinylidene groups, conjugated with ester or amide structures.. The following specific compounds are further illustrative of this class: unsaturated esters of polyols, particularly such esters as the α-methylene carboxylic acids, e.g., ethylene diacrylate; diethylene glycol diacrylate; glycerol diacrylate; glycerol triacrylate; ethylene dimethacrylate; 1,3 - propanediol dimethacrylate; 1,2,4-butanetriol trimethacrylate; 1,4-benzenediol dimethacrylate; 1,4-cyclohexanediol diacrylate; pentaerythritol tri- and tetramethacrylate; pentaerythritol tetraacrylate; 1,3-propanediol diacrylate; 1,5-pentanediol dimethacrylate; the bis-acrylates and methacrylates of polyethylene glycols of molecular weight 100-1500 and the like; unsaturated amides, particularly those of the α-methylene

carboxylic acids, and especially those of alpha, omega-diamines and oxygen-interrupted omega-diamines, such as methylene bisacrylamide; methylene bis-methacrylamide; 1,6-hexamethylene bisacrylamide; diethylene triamine tris-methacrylamide; bis (methacrylamidopropoxy) ethane; β-methacrylamidethyl methacrylate; and N-[(β-hydroxyethyloxy) ethyl] acrylamide.

In a preferred embodiment the ethylenically unsaturated addition polymerizable compound is an acrylyl or methacrylyl compound or derivative thereof, including low molecular weight polymerizates, i.e., oligomers. Particularly useful results are obtained when the dry film photoresist composition contains a preferred curable or crosslinkable polymer or oligomer and an acrylyl ester as the ethylenically unsaturated addition polymerizable compound. The acrylyl esters that are particularly useful are the mono- and polyacrylyl compounds of general formula:

$$CH_2{=}\overset{\overset{\displaystyle M}{|}}{C}{-}COOM' \quad \text{or} \quad (CH_2{=}\overset{\overset{\displaystyle H}{|}}{C}{-}COO)_rG$$

Where the acrylyl compound has the formula

$$CH_2{=}\overset{\overset{\displaystyle M}{|}}{C}{-}COOM'$$

M is H or CH_3

M' is cycloalkyl of 5 to 12 carbon atoms (such as cyclopentyl, dicyclopentyl, methyclyclopentyl, dimethylcyclopentyl, etc.)

cycloalkenyl of 5 to 12 carbon atoms (such as cyclopentenyl, methylcyclopentenyl, dicyclopentenyl, bicyclo [2.2.1] hept-2-en-yl, etc.)

$-C_pH_{2q}M''$ or

$(C_qH_{2q}O)_1C_qH_{2q+1}$

where

p is an integer from 1 to 10

q is an integer from 2 to 4

s is an integer from 0 to 4

M" is hydrogen, hydroxyl, phenoxy, alkoxy of 1 to 8 carbon atoms;

and where the acrylyl compound has the formula:

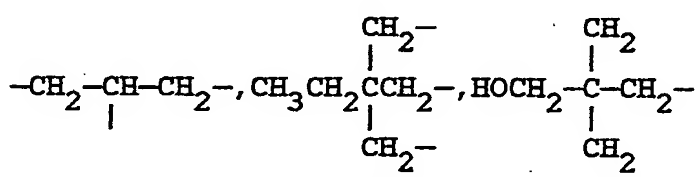
$$(CH_2=\overset{\overset{\displaystyle H}{|}}{C}-COO),G$$

G is a polyvalent alkylene group of formula $-C_2H_{2x-y}-$ in which

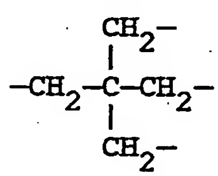
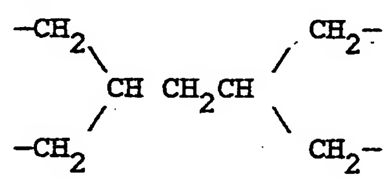
x is an integer from 2 to 8

y is an integer from 0 to 2

(for example, divalent alkylene when y = 0 such as $-C_2H_4-$, C_3H_6-iso$-C_3H_6-$, $-C_5H_{10}-$, neo$-C_6H_{12}$ etc; trivalent alkylene when y = 1 such as



or tetravalent alkylene when y is 2, such as

 and 

etc.)

or G is a divalent ether or ester group of formula

$$-(C_qH_{2q}O)_1C_qH_{2q}- \quad \text{or}$$

$$-(C_qH_{2q}COO)_tC_qH_{2q}-$$

where t is an integer from 1 to 5 and q is an integer from 2 to 4 (such as oxyethylene, oxypropylene, oxybutylene, polyoxyethylene, polyoxypropylene, polyoxybutylene, etc.) and r is the valence of G and can be 2 to 4.

Especially preferred acrylyl compounds are triethylene glycol diacrylate, tetraethylene glycol diacrylate, pentaerythritol triacrylate, trimethylol propane triacrylate and pentaerythritol tetraacrylate.

As preformed polymeric binding agent there can be employed polystyrene, polycarbonate, polyurethane, polyformaldehyde, polyvinyl acetal (including polyvinyl butryal), polyvinyl chloride and copolymers, polyethers (including polyethylene oxide, polypropylene oxide, polytetrahydrofuran), polyacrylates (including polymethyl methacrylate, polyethyl methacrylate, polymethyl acrylate and polyethyl acrylate), polyvinyl esters (including polyvinyl acetate and polyvinyl acetate/acrylate), cellulose esters (including cellulose acetate and cellulose acetate butyrate), cellulose ethers (including methyl cellulose and ethyl cellulose), modified polyolefins (including ethylene/vinyl acetate copolymers) polyvinylidene chloride (including copolymers of vinylidine chloride with acrylonitrile, methyl methacrylate and vinyl acetate), polyamide (including polycaprolactone, polycaprolactam, and polyhexamethylene adipamide) and polyester (including polyethylene glycol terephthalate, and polyhexamethylene succinate).

Photoinitiators used in the compositions are preferably those that are activated by actinic light and

thermally inactive at 185°C. or below. These include the substituted or unsubstituted polynuclear quinones, such as, 9,10-anthraquinone; 1-chloroanthraquinone, 2-chloroanthraquinone, 2-methylanthraquinone; 2-ethylanthraquinone; 2-tert-butylanthraquinone; octamethylanthraquinone; 1,4-napththaquinone; 9,10-phenanthraquinone; 1,2-benzathraquinone; 2,3-benzanthraquinone; 2-methyl-1, 4-napthaquinone; 2,3-dichloronaphthaquinone; 1,4-dimethylanthraquinone; 2,3-dimethylanthraquinone; 2-phenylanthraquinone; 2,3-diphenylanthraquinone; 3-chloro-2-methylanthraquinone; retenequinone; 7,8,9,10-tetrahydronaphthacenequinone; 1,2,3,4-tetrahydrobenz(a)-anthracene-7,12-dione.

The following photoinitiators, described in U.S. Pat. No. 2,760,863, some of which may be thermally active at temperatures as low as 85° C. are also useful: vicinal ketaldonyl compounds, such as, diacetyl and benzil; alpha-ketaldonyl alcohols, such as, benzoin and pivaloin; acyloin ethers, e.g., benzoin methyl and ethyl ethers; α-hydrocarbon substituted aromatic acyloins; α-methylbenzoin; α-allylbenzoin; and α-phenylbenzoin.

Specific benzoin ethers include benzoin methyl ether, benzoin ethyl ether, benzoin phenyl ether, methylbenzoin; and ethylbenzoin.

Certain aromatic ketones, e.g., benzophenone and 4,4'-bis-(dialkylamino)benzophenones, are also useful. Specific compounds include benzophenone, 4,4'-bis(dimethylamino)benzophenone, 4,4'-bis(diethylamino)-benzophenone, 4-hydroxy-4'-diethylaminobenzophenone, 4-hydroxy-4'-dimethylaminobenzophenone, 4-acryloxy-4'-dimethylaminobenzophenone, and 4-methoxy-4' dimethylaminobenzophenone.

The initiator preferably contains at least one of an acyloin ether, an alkyl-substituted anthraquinone where said alkyl group contains one to four carbon atoms, benzophenone or an alkylaminobenzophenone.

Thermal polymerization inhibitors are also present in the preferred compositions. These include p-methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, naphthylamines, β-naphthol, 2,6-di-tert-butyl p-cresol, 2,2'-methylene-bis-(4-ethyl-6-t-butylphenol), pyridine, nitrobenzene, dinitrobenzene, p-toluquinone, chloranil, aryl phosphites, and aryl alkyl phosphites.

The photoresist compositions will normally be formulated in a suitable solvent, usually an organic solvent, such as a ketone of from three to six carbon atoms, by themselves or in combination with alkanols of from one to three carbon atoms, or the like, wherein the percent solids will generally vary from about 10 to 50 weight percent.

The compositions of this invention can be supplied laminated onto a copper sheet, normally a laminate having a top copper layer in contact with the uncured photoresist composition. A protective film for the photoresist layer may also be provided resulting in a sandwich of the protective film, the uncured photoresist layer and the copper layer. The photoresist layer will generally have a dry thickness of from about 0.25 to 5, usually 0.75 to 4.0 mils thickness. The protective layer will generally be from about 0.5 to 5 mils thickness and may be an inert addition or condensation polymer, such as polyolefins of from 2 to 4 carbon atoms, e.g. polypropylene, polyethylene terephthalate, or the like.

In use, the photopolymerizable dry film is exposed to a source of actinic radiation which may be through a half-tone image or a process transparency; e.g., a process negative or positive, stencil or a mask. Exposure may also be through a continuous tone, negative or positive image. The exposure can be by the contact or

projection method, with or without a cover sheet over the photopolymerizable layer or by projection using a cover sheet. These procedures are well known to those skilled in the art. The photoresist compositions are generally used in conjunction with ultraviolet light and the radiation source should furnish an effective amount of this radiation; point or broad radiation sources are effective. Such sources include carbon arcs, mercury-vapor arcs, fluorescent lamps with ultraviolet radiation emitting phosphors, argon glow lamps, electronic flash units and photographic flood lamps. Of these, the mercury vapor arcs, particularly the sun lamps, are most suitable.

The dry film photoresist compositions after exposure can be developed in known manner, for example by impingement of spray jets, with agitated immersion brushing or scrubbing to desirable images with an organic solvent or mixture thereof capable of washing away the unexposed portions of the resist film. Useful solvents include cellosolve acetate, ethyl acetate, methyl ethyl ketone, acetone, tetrachloroethylene, the alkanols of one to four carbon atoms, butyl cellosolve, chlorobenzene and dimethylformamide or water or mildly alkaline solution, which may contain small amounts of organic additives.

Besides use in photoresist compositions, the subject compositions can also find application in ultraviolet, curable coding and printing compositions. These compositions will for the most part have a free-radical addition polymerizable monomer, a photoinitiator, and the print out dye composition of this invention, in addition to other specialized additives, which have been previously described. These compositions will generally have from about 0.1 to 6, more usually from about 0.2 to 5 weight percent of the subject print out dye composition.

While the ethylenically unsaturated compounds previously described are useful, the acrylyl compounds are particularly useful, especially in the form of acrylyl oligomers and esters, as described above.

One useful class of oligomers is obtained by reacting an organic polyether or polyester polyol with a diisocyanate to provide an isocyanate-terminated prepolymer. This product can be reacted with an unsaturated alcohol, such as a hydroxyalkyl acrylate to provide, either alone or in combination with other unsaturated monomers, a material that will polymerize under the influence of free radicals to form a hard, tough, adherent film.

In a variation of the foregoing, a polymercaptoester such as trimethylolpropane tris(thioglycolate); trimethylolpropane tris(mercaptopropionate); pentaerythritol tetrakis(thioglycolate); pentaerythritol tetrakis(mercaptopropionate); and the like are reacted with a diisocyanate to provide a polythiourethane intermediate which can be reacted with an unsaturated alcohol, such as a hydroxyacrylate to provide, either alone or in combination with other unsaturated monomers, a free radical polymerizable material having excellent film properties after crosslinking.

Another illustration of a useful oligomer is an acrylate-capped polycaprolactone polyurethane, obtained by reacting a hydroxy terminated polycaprolactone with a diisocyanate and thereafter reacting the isocyanate terminated intermediate with an unsaturated alcohol such as a hydroxyalkyl acrylate.

Still another useful class of oligomers is obtained by reacting an epoxy resin with acrylic acid to obtain an epoxy diacrylate. For example, an epichlorohydrin/bisphenol A-type epoxy resin can be reacted with a stoichiometric amount of acrylic acid. Such products are

available commercially as under the trademark "Epocryl" from Shell Chemical Company. Alternatively, one could use Vcar-80 from Union Carbide Company. Such materials can be combined with a variety of acrylic esters including neopentylglycol diacrylate, hydroxyethyl acrylate and dicyclopentenyl acrylate and other unsaturated esters of polyols including such esters of methylene carboxylic acid such as, ethylene diacrylate; diethyleneglycol diacrylate; glycerol diacrylate; glycerol triacrylate; ethylene dimethacrylate; 1,3-propylene dimethacrylate; 1,2,4-butanetriol trimethacrylate; 1,4-benzenediol dimethacrylate; pentaerythritol tetramethacrylate; 1,3-propanediol diacrylate; 1,6-hexanediol diacrylate; the bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200-500; trimethylolpropane triacrylate; pentaerythritol triacrylate; and other ethylenically unsaturated compounds, to polymerize under the influence of free radicals to form films of excellent adhesion and toughness.

Another composition comprises a combination of a terminally unsaturated urethane composition (polyene) and a polythiol which are polymerizable under the influence of free radicals generated by the action of actinic light on a photoinitiator.

The coating and printing ink compositions will contain a predominant amount of film forming materials and photosensitizer and a relatively minor amount of leuco dye and halogen compound. For example, a typical composition will contain from 15 to 70% by weight of an ethylenically unsaturated compound as described above, 10-50% of one or more unsaturated monomers or of a preformed polymeric binder, 0.1 to 15% by weight of a photoinitiator; 0.01 to 3% by weight of leuco dye as described above and 0.1 to about 5% of halogen containing compound. A more narrow range is from about 40 to about 55% of

ethylenically unsaturated compound, from 30-45% of monomer or of polymeric binder from 0.5 to 15% of total initiator, from 0.5 to 2% of dye base and from 0.8 to 4% of halogen compound (all % by weight).

The photoresist compositions are frequently provided as a laminated sandwich, with the photoresist layer between two strippable polymeric films. One of the films should be substantially transparent to actinic light. The films will normally be from about 0.25 to 10 mils thickness.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE I

The following photopolymerizable composition was prepared:

Acrylic polymer (56% ethyl acrylate, 37% methyl methacrylate and 7% acrylic acid, with an inherent viscosity of 0.458 in methyl ethyl ketone at 30° C.)	12.63 gram
Styrene-Maleic anhydride co-polymer, partially esterified with acid number of 270 and a molecular weight of 1700.	12.63 "
Triethyleneglycol dimethacrylate	6.67 "
Benzophenone	1.30 "
4,4'-bis(dimethylamino)benzophenone	0.067 "
Brilliant Green dye (C.I. 42040)	0.0027 "
Leuco Crystal Violet	0.39 "
1,2,3,4,5,-pentabromo-6-chlorocylohexane	0.63 "
Methyl ethyl ketone	100.00 "

The solution contained about 25% solids, and was coated with a "doctor knife" on 0.00092 inch thick, biaxially oriented and heat set polyethylene terephthalate film. The coating was air dried resulting in a very light green film with a dry thickness of 0.00130 inches.

A piece of copper clad epoxy-fiberglass board is scrubbed and dried using a Somaca Model SBC-12G scrubber. The copper board is laminated with the dried photopolymerizable composition using a Xidex laminator at 115°C, at a rate of 3-4 feet per minute. The resulting composite of polyester film, photopolymerizable composition, and copper has a slight green color with sufficient contrast under yellow light to discern any bare copper. The copper sandwich is exposed for 10 seconds, to a transparency, using a Colight 1200 watt DMVL-A ultraviolet exposure source. Immediately after exposure a strong purple image is formed in the exposed areas which have excellent contrast with the light green background. The board is developed in a DEA Americana 2401 developer with a 30" spray chamber. The totally aqueous developer contains 0.75% by weight sodium carbonate monohydrate at 80-85°F. Using a spray pressure of 20 pounds per square inch and a throughput rate of 3.5 feet per minute, the board is passed through the developer. After rinsing and drying, the remaining exposed image has a strong color which has remained virtually unchanged since exposure. The board is dipped for 1 minute in 20% ammonium persulfate solution, rinsed with large amounts of water, dipped in a 20% solution of HCl for 1 min, again rinsed with water and then plated for 45 minutes in an acid copper sulfate bath at 25 amperes per square foot, at ambient temperature. After plating, no discernible color change of the resist image had taken place. The board was again rinsed, dipped for 1 minute in 15% fluoboric acid and then plated for 30 minutes in a Pb/Sn plating bath using 15 amperes per square foot at ambient temperatures. As before, no discernible change in color was observed. The purple resist image was stripped by dipping in 3.0% by weight KOH solution at 40°C for 40 seconds. After rinsing the board was etched in $FeCl_3$

solution which removed any unprotected copper to give a useable electronic circuit board.

Example II

The composition of Example I was used, except that the print out dye employed was an equal amount of leuco Malachite Green and the other dye, an equal amount of Pararosaniline Acetate (C.I. 42500). After coating, the composition had a slight red color which gave good contrast under yellow light with the dark green print-out image that resulted after exposure. The board was again developed under the same conditions, but the exposed copper was then etched away in a DEA etcher containing Ac-Cu Guard etching solution at a pH of 8.7 and a temperature of 45°C. The board passed through the six foot etching chambers at the rate of 6 feet per minute. Although the resist had dulled slightly, the color was virtually unchanged.

Example III

Example I was repeated, except that the 1,2,3,4,5-pentabromo-6-chlorocylohexane was replaced by an equivalent amount of dibromoneopentyl glycol. Similar results were obtained.

Example IV

Example I was repeated, except that the 1,2,3,4,5,-pentabromo-6-chlorocyclohexane was replaced by an equivalent amount of pentaerythrityltetrabromide. The results were virtually the same.

Example V

The following photopolymerizable composition was prepared:

Poly(methylmethylmethacrylate) inh. vis. in methyl ethyl ketone at 30°C=0.380	9.36 gram
Trimethylolpropane triacrylate	2.50 "
Tetraethyleneglycol dimethacrylate	2.50 "
Dioctylphthalate	0.10 "
Benzophenone	0.85 "
4,4'-bis (dimethylamino) benzophenone	0.030 "
4-methyl-2,6-di-t-butylphenol	0.002 "
Brilliant Green Dye (C.I. 42040)	0.002 "
2-mercaptobenzothiazole	0.010 "
1,2,3,4,5-pentabromo-6-chlorocyclohexane	0.255 "
Leuco Pararosaniline	0.175 "
Methyl ethyl ketone	33.0 "

The solution was coated to a dry thickness of 1.5 mil on 0.00092 inch thick poly(ester) film. It was then laminated as in Example I to clean copper clad laminate. The film was exposed for 15 seconds in the DMVL-A which resulted in a strong red print-out on a green background. The exposed board was held at room conditions for 15 minutes and then developed in 1,1,1-trichloroethane at 7 feet/minute, at 68°F. After drying the board was pre-plate cleaned as in Example I. It was then plated at 125°F. in a copper-pyrophosphate plating bath for 45 minutes using 25 amperes per square foot. After plating the board was inspected for loss in color: no loss was observed. A second formulation not using 2-mercaptobenzothiazole gave similar results, except that the adhesion of the resist after plating was poor.

Example VI

The following photopolymerizable composition was prepared:

Acrylic polymer with an inherent viscosity of 0.11 in methyl ethyl ketone at 30°C. Acid number of 55-60.	21.00	gram
Trimethylolpropane triacrylate	3.30	"
Triethyleneglycol dimethacrylate	3.30	"
Benzophenone	1.75	"
4,4'-bis (dimethylamino)benzophenone	0.092	"
4-methyl-2,6-di-t-butylphenol	0.0014	"
Basic Blue 26 (C.I. 44045)	0.0040	"
Brilliant Green	0.0008	"
Leuco Crystal Violet	0.300	"
1,2,3,4,5,-pentabromo-6-chlorocyclohexane	0.50	"
Methyl ethyl ketone	50.00	"
Methanol	2.00	"

The solution was coated as previously to a dry thickness of 0.00150 inches on 0.00092 inch thick poly (ester) base. After drying, three pieces were laminated to 3 5"x 6" 1 oz. copper clad epoxy-fiberglass boards. A fourth piece was laminated with 0.0010 inch thick poly (ethylene). This piece of film was taped to the wall for later use. One copper board was placed in a Blue M Oven for three days at 35-38°C. A second board was placed in a drawer at ambient temperatures, while the third board was exposed and developed as in Example I. A dark purple print-out image resulted with a photospeed of 9√2 steps on a standard stepwedge tablet. A similar composition was prepared, except that the halogenated cyclohexane was replaced by 0.32 g. carbon tetrabromide. After exposure and development a similar purple image was obtained showing 10√2 steps. After three days in the oven or three weeks at room temperature (both on the copper and in polyethylene laminated sample) there was no change in

photospeed or printout image density using the brominated cyclohexane derivative. Nor had the film color darkened as measured by a Perkin Elmer 402 Ultraviolet spectrophotometer. In the formulation where carbon tetrabromide was substituted for the halogenated cyclohexane, the following occurred: the sample in the oven had turned completely purple, and no print-out image was formed upon exposure. The photospeed had dropped by 2√2 steps. The sample on copper which had been stored in the drawer gave a slight print-out image over the darker background, with a similar loss in photospeed. The sample laminated with polyethylene had increased by a factor of 2.5 in background density and had lost 1√2 steps. Similar results were obtained when 2',3',4'-trichloroacetophenone, N-chlorosuccinimide or iodoform were used.

Example VII

A coating composition was prepared from the following ingredients:

Actomer X-80 (epoxidized soya bean oil from Union Carbide)	30.00 gram
Trimethylolpropane triacrylate	20.00 "
Pentaerythritol triacrylate	10.00 "
Vinyl Acetate	20.00 "
Benzophenone	12.00 "
4,4'-bis(dimethylamino)benzophenone	1.0 "
1,2,3,4,5-pentabromo-6-chlorocyclohexane	1.5 "
Leuco Crystal Violet	1.0 "

The solution was coated on a piece of cardboard with a 10 mil "doctor knife." The tacky coating was then exposed to a high intensity ultraviolet light source for 60 seconds (DMVL-A, 1200 Watt bulb). A deeply colored tough scratch resistant film was obtained which could not be attacked with methanol or 1,1,1,-trichloroethane.

As evidenced by the above results, use of the print out dye compositions of the subject invention provide for excellent results in the production of photopolymerizable compositions. The dyes do not interfere with the photocuring of the polymers, so that a stable coating is obtained. Furthermore, the compositions can be stored for long periods of time either as formulations or uncured films, without affecting the properties of the compositions. In addition, the print out dye compositions do not produce noisome or dangerous fumes during processing, nor is there any evidence of lachrymatory effects. Finally, the desired color is retained to provide the necessary contrast during subsequent processing.

WHAT IS CLAIMED IS:

1. A contrast colorant for photopolymerizable compositions comprising in combination a leuco triarylmethane dye in combination with a sufficient amount for formation of the colored form of said dye upon irradiation with actinic light of a bromine or chlorine substituted neoalkane or cycloalkane.

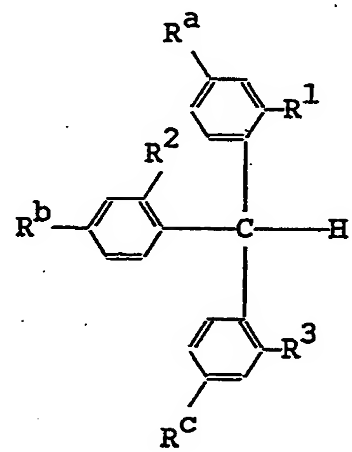
2. A composition according to claim 1, wherein the mole ratio of said dye to said substituted neoalkane or cycloalkane is 0.2-5:1.

3. A composition according to any of Claims 1 and 2, wherein said triarylmethane leuco dye has at least one amino substituent.

4. A composition according to any of Claims 1 and 2 wherein said bromocycloalkane is a cycloalkane of from 5 to 6 annular carbon atoms having up to 5 bromine atoms other than geminal substituted.

5. A composition according to any of Claims 1 and 2, wherein said substituted compound is neoalkane having from 2 to 4 bromine or chlorine atoms other than geminal substituted.

6. A colorant composition for use in photopolymerizable compositions comprising in combination for about 0.2-5 moles of a triarylmethane leuco dye of the formula:

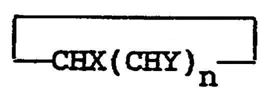


wherein:

R^{a-c} are the same or different and are hydrogen, amino, oxy, alkyl, or halo; and

R^{1-3} are the same or different and are hydrogen, amino, oxy, alkyl or halo; and

a cycloalkane of the formula,



wherein:

the Y's may be the same or different and are hydrogen, bromine, or chlorine; and

n is 4 to 7 or a neoalkane of the formula:

$C(CH_2X)_p(CH_2Z)_{4-p}$

wherein:

X is chloro or bromo;

Z is hydrogen of hydroxyl; and

p is 2 to 4.

7. A composition according to Claim 6, wherein R^{1-3} are hydrogen; and

from 1 to 3 of R^{a-c} are dimethylamino and are otherwise hydrogen; and

said compound is a cycloalkane wherein n is 5, four of the Y's are bromine and one of the Y's is chlorine.

8. A composition according to Claim 6, wherein R^{1-3} are hydrogen; and

from 1 to 3 of R^{a-c} are dimethylamino and are otherwise hydrogen; and

the compound is a neoalkane wherein p is 2 to 4 and Z is hydroxyl.

9. A photopolymerizable composition comprising:

(1) an addition polymerizable photo initiator;

(2) a polymeric binder;

(3) a polymerizable monomer capable of photopolymerization initiated by said photo initiator;

(4) a composition according to Claim 1.

10. A composition according to claim 9, wherein said polymeric composition includes an acrylate at least in part and said monomer includes an acrylate at least in part.

11. A composition according to claim 9, wherein said polymer includes an epoxy at least in part and said monomer includes an acrylate at least in part.

12. A photopolymerizable composition comprising from about 40 to 70 weight percent of a polymeric binder; from about 0.01 to 10 weight percent of a photoinitiator; from about 30 to 50 weight percent of an addition polymerizable monomer capable of photoinitiated polymerization by said photoinitiator, and a composition according to any of claims 1, 2 and 5-8, wherein said leuco dye is present in from 0.01 to 2 weight percent of the total composition and said substituted compound is in from 0.1 to 4 weight percent of the total composition.

13. A composition according to claim 12, wherein said composition is a solution in an organic solvent having from about 10 to 50 weight percent solids.

14. A composition according to claim 12, wherein said composition is coated, has a layer on a copper layer of a thickness in the range of about 0.25 to 5 mils.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 79/00888

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.[3] G03C 1/52
U.S. CL. 430/344

WO 80/01846

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	430/344, 281, 292, 925

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 3,525,616, Published 25 AUGUST 1970, See column 2, lines 5-21, HACKMANN	1
X	US, A, 3,769,023, Published 30 OCTOBER 1973, LEWIS	1
A	US, A, 3,113,024, Published 03 DECEMBER 1963, SPRAGUE	1
A	US, A, 3,712,817, Published 23 JANUARY 1973, HAZY	1
A	US, A, 4,065,315, Published 27 DECEMBER 1977, YAMAZAKI	1

* Special categories of cited documents: [15]

"A" document defining the general state of the art
"E" earlier document but published on or after the international filing date
"L" document cited for special reason other than those referred to in the other categories
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but on or after the priority date claimed
"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention
"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
15 FEBRUARY 1980	20 MAR 1980
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	WON H. LOUIE

Form PCT/ISA/210 (second sheet) (October 1977)